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Molecular structure, vibrational spectra and NMR analyses on two azopyridine ruthenium complexes using density functional theory calculations

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ABSTRACT

$RuCl_2(Azpy)_2$and $RuCl_2(Nazpy)_2$ are two bidentatesazopyridineruthénium(II) complexes that were characterized by DFT calculation. Azpy and Nazpy stand respectively for 2-phenylazopyridine and 2-phenylazonaphtol. Several levels of prediction were performed comprising the functional hybrid B3LYP with LANL2DZEffective Core Potential (ECP) basis set either in gas or in condensed phase. Actually, five isomers are by experiment obtainable since azopyridine ligands are not symmetrical. But the synthesis that gathers $RuCl_3,3H_2O$ with a ligand produces only two isomers named γ-Cl and δ-Cl. Both isomers are C_2 symmetrical and the most abundant is assumed to be γ-Cl. The particularity ofδ-Cl is that both chlorine atoms are different. Besides, while symmetry is through the bisector of N_{py}-Ru-N_{py} angle in γ-Cl, it is however seen through the axis Cl-Ru-Cl in δ-Cl. Moreover, the ^1H NMR calculation shows up that LANL2DZ effective core potential basis set provides chemical shifts that match with experiment data and requires to be exploited in gas phase. Furthermore, frequency calculations at 298.15K show up that the most stable isomer is δ-Cl. Nevertheless, when synthesis is performed at high temperature, the most profitable isomer becomes γ-Cl.

Keywords: DFT prediction, Pseudo-potential, Azopyridine, Complexes of ruthenium, Relativistic effect.

INTRODUCTION

The use of azopyridine molecules as ligand to perform ruthenium complexes is of real interest since they have been discovered to provide with low number of oxidation Ru(II) and Ru(III) [1-3]. This fact permits them to be used not merely as sensitizers in solar cell and in photochemistry reaction comparatively to bipyridine ligands [4, 5]but also as catalysts to oxidize selectively high value molecules [6, 7]. In our first paper, we demonstrated by hydrogen-bond basicity calculation that azopyridine ligands (Azpy, Dazpy, Mazpy and Nazpy)are bidentates. Thus, they bind to metal by the same two atomic centers forming a five-ring stable complex [8].From now on, we assume that all azopyridine ligands behave like the aforementioned ones. Therefore, Figure 1 displays the common structure regarding both Azpy and Nazpy ligands.

Regarding their experimental synthesis, the main method used as $RuCl_3,3H_2O$ reacting with azopyridine ligand in methanol phase, under reflux at high temperature, leads to two C_2 symmetrical isomers that are characterized as trans-transor δ-$RuCl_2(Ligand)_2$ and cis-trans or γ-$RuCl_2(Ligand)_2$up to now respectively named δ-Cl and γ-Clisomers as highlighted in Figure 2. The common structure of the complex is therefore written as $RuCl_2(Ligand)_2$ where ligand stands for azopyridine and the presence of the C_2 axis renders both ligands molecules equivalent in the complex. Henceforth, the investigated complexes are $RuCl_2(Azpy)_2$and $RuCl_2(Nazpy)_2$ respectively. As they are concerned, $RuCl_2(Azpy)_2$[8-12]has widely been studied, whereas $RuCl_2(Nazpy)_2$,it has been slightly mentioned in literature [13]. Regarding the hindering shape of the ligand, both isomers are produced with the most different ratio. For instance, when $RuCl_2(Azpy)_2$ was synthesized [3], isomer γ-Cl was obtained with 95% of yield. Whereas the

others existing isomers named α-Cl, β-Cl and ε-Cl, they are formed by using the former synthesized isomers as new reactives [14]. In this paper, we aim to optimize through DFT investigation, at B3LYP level with LANL2DZ effective core basis set, both γ-Cl and δ-Cl complexes performed with both ligands. Moreover, we need to calculate their energy so as to know the most stable complex and to check out the consistency with experimental data. Then, ^{1}H NMR spectroscopy was performed to know the structure of each complex.

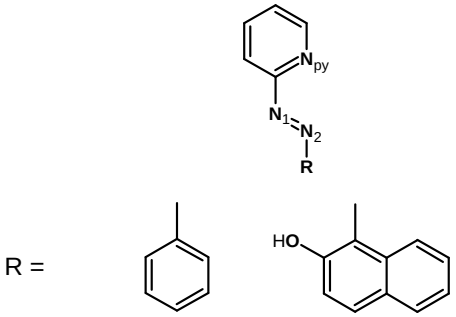

Figure 1: Common structure of both Azpy and Nazpy ligands. The ligands bind to the metal by N_{py} and N_2 atoms. Azpy corresponds to the ligand where R stands for phenyl ring. Thus, it corresponds to 2-phenylazopyridine. Nazpy stands for 2-phenylazonaphtol. Herein, R represents the naphtol ring

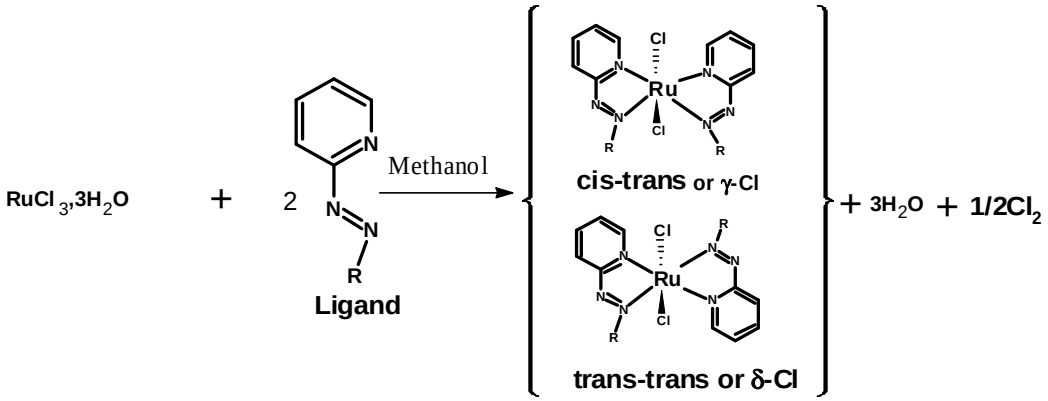

Figure 2: Synthesis of azopyridine ruthenium complexes. In this paper, when phenyl ring replaces R, we have Azpy ligand. Whereas Nazpy ligand it corresponds to R replaced by 2-hydroxy naphtyl group. In both structure, chlorine atoms are in trans position

EXPERIMENTAL SECTION

All calculations were performed on the optimized geometry of each complex. The optimized geometry was undertaken at B3LYP/LANL2DZ levels. LANL2DZ basis set is known to be an effective core potential (ECP) which is admitted to display accurate result with transition metals. Besides, it is also suitable for any atom from the periodic table. Furthermore, concerning others calculations on the optimized molecules like ^{1}H NMR and vibrational frequency, more others ECPs basis set were also tested. All the calculations were performed using Gaussian 03 program package [15].^{1}H NMR was calculated at B3LYP/LANL2DZ. Regarding ruthenium complexes, separate basis set were also considered where ruthenium atom was treated at LANL2DZ [16-18] and all others atoms were calculated at B3LYP/6-31g(d). The latter 6-31g(d) basis set is admitted to provide with accurate results regarding ^{1}H NMR of molecules containing only light atoms [8].

RESULTS AND DISCUSSION

3.1. Geometry optimization and frequency calculation

3.1.1. Geometry optimization

Throughout frequency calculations in addition to FTIR determination of the main bonds like organometallic and azobonds, variation of free enthalpy was determined to find out which isomer of a complex is the most stable in relation to Figure 2.Table 1displays selected bonds of azopyridine ruthenium complexes that characterize the organometallic bonds. It can be observed that all γ-Cl isomers present single value for each bond. This result demonstrates that γ-Cl isomers are absolutely symmetrical through both azopyridine ligands and both chlorine atoms. However, the isomers δ-Cl show two values belonging to Ru-Cl bonds. It means that both chlorine atoms are not in the same environment. Thus, they are not symmetrical. Nevertheless, the Cl-Ru-Cl angle in δ-Cl isomers is

180°. It confirms that in addition to a plan, a C_2axis divides up the complexes where both azopyridine ligands turn out equivalent. In consequence, their geometry is assumed to be C_2 type. Regarding γ-Cl isomers, the Cl-Ru-Cl angles are lower than 180°. This distortion that maintains the symmetry of the complex must certainly be due to Yahn-Teller effect[18].Thus, both ligands are symmetrical thanks to a C_2 axis that passes through the bisector of N_{py}-Ru-N_{py} and N_2-Ru-N_2 angles. Particularly, this C_2 axis renders both chlorine atoms also symmetrical in addition to the ligands. It follows that the geometry of these isomers is also C_2 type. Herein, Figure 3 displays by instance both γ-Cl and δ-Cl isomers of $RuCl_2(Nazpy)_2$ to emphasize the general structure. Moreover, γ-Cl isomers seem to be the most stable in both $RuCl_2(Azpy)_2$ and $RuCl_2(Nazpy)_2$ though their Ru-Ligand bonds are shorter than those of δ-Cl isomers. Regarding azo bonds, there are invariable either in γ-Cl or δ-Cl no matter how the shape of the ligand can be. In all case, δ-Cl is the isomer that exhibits the shortest value with 1.31Å as commented Velders et al [14].

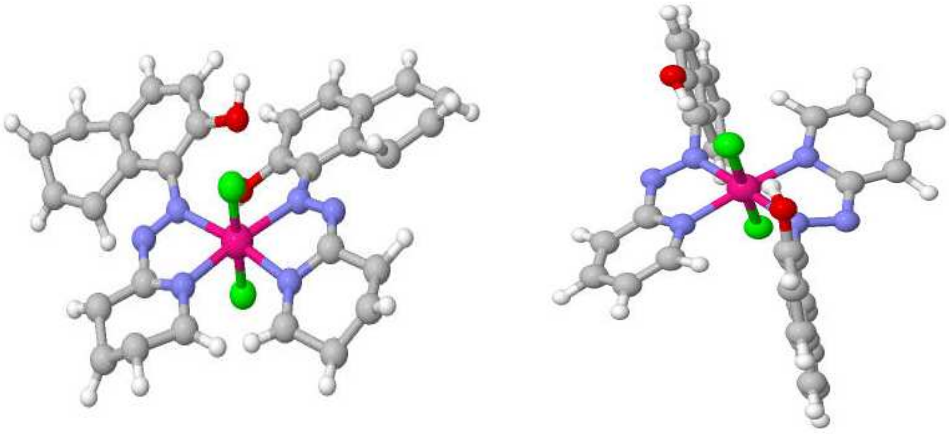

Figure 3: γ-$RuCl_2(Nazpy)_2$ and δ-$RuCl_2(Nazpy)_2$ displaying C_2 axis that renders either both Azpy and both Cl equal according to the isomers

Table 1: Selected geometrical parameters calculated for both isomers γ-Cl and δ-Cl of $RuCl_2(Azpy)_2$ and $RuCl_2(Nazpy)_2$at 3LYP/LANL2DZ level. Distances are reported in Å and angles in °

Parameters	$RuCl_2(Azpy)_2$		$RuCl_2(Nazpy)_2$	
	γ-Cl	δ-Cl	γ-Cl	δ-Cl
Ru-Cl	2.48	2.51-2.49	2.49	2.53-2.48
Ru-N_2	2.03	2.06	2.07	2.08
Ru-N_{py}	2.10	2.10	2.08	2.10
N=N	1.32	1.31	1.32	1.31
Cl-Ru-Cl	170.71	180.00	169.79	180.00
Cl-Ru-N_2	90.29-95.36	89.29-90.71	88.07-98.16	89.95-90.05
Cl-Ru-N_{py}	85.02-89.19	83.76-96.23	86.7-86.92	88.55-91.45
N_2-Ru-N_2	104.99	178.58	104.99	179.9
N_2-Ru-N_{py}	76.07-178.86	76.28-103.88	76.44-174.73	76.68-103.32
N_{py}-Ru-N_{py}	102.86	167.53	102.61	177.10

[a]γ-$RuCl_2(Azpy)_2$ was characterized by Velders et al.[19] and the experimental data are respectively Ru-Cl 2.37; Ru-N_2 1.99; Ru-N_{py} 2.10; Cl-Ru-Cl 170.50; Cl-Ru-N_2 88.88-96.87; Cl-Ru-N_{py} 85.71-88.64; N_2-Ru-N_2 103.80; N_2-Ru-N_{py} 75.80-177.52; N_{py}-Ru-N_{py} 104.10

3.1.2. Frequency calculation

Vibrational data are divided up in two regions. The first one regards the region 100-400cm^{-1} performed experimentally in polyethylene disk deals with metal-ligand bonds. The second region is performed in KBr disk. It concerns the 400-4000cm^{-1} region. Herein, stretching data are seen only within ligands. Table 2 collects stretching frequencies calculated for both complexes at B3LYP/LANL2DZ level. As mentioned above, both isomers belonging to each complex are C_2 symmetrical. In consequence, vibrational data must be identical by pair. Herein, allγ-Cl isomers present only one data for each bond confirming their full symmetry. Whereas the δ-Cl isomers, they display two values regarding Ru-Cl stretching. This result explains that both chlorine atoms in those isomers are not in the same environment. Therefore, they are not symmetrical. Nevertheless, δ-Cl isomers display their symmetry through a plan and an axis that comprise the three Cl, Ru and Cl atoms. Besides, in azopyridineruthenium complexes, vibrations of Ru-N are always present in the region 200-300 cm^{-1}apart from $RuCl_2(Nazpy)_2$ where Ru-N vibration is above 300 cm^{-1}. Moreover, vibrations regarding Ru-Cl are in the region 300-400cm^{-1} and the vibration concerning azo group appears in the region 1300-1400 cm^{-1} as shown Velders et al [14]. In addition, vibration of double bonds C=N and C=C stretch both in The region 1600-1700cm^{-1}. Those data have all shifted when azopyridine ligands are

lonely considered. Here, N=N stretching is almost between 1400 and 1500 cm^{-1}. Whereas both C=N and C=C stretching, they remain the same with slight modifications. We can assume here that only N=N bonds are affected by the presence of Ru atom.

Table 2: Vibrational data in cm^{-1} calculated at B3LYP/LANL2DZ level on azopyridine ligands and on their corresponding ruthenium complexes comprising both isomers.

Vibration modes	$Ru(Azpy)_2Cl_2$		$Ru(Nazpy)_2Cl_2$		Azpy	Nazpy
	γ-Cl	δ-Cl	γ-Cl	δ-Cl		
ν(Ru-Cl)	315.5	305.0-319.4	308.7	255.6-309.0		
$\nu(Ru-N_2)$	238.3	220.0	328.9	322.2		
$\nu(Ru-N_{py})$	285.1	258.9	306.6	295.1		
ν(N=N)	1333.4	1374.5	1337.0	1373.4	1454.3	1432.1
ν(C=N)	1594.9	1595.2	1593.1	1597.1	1603.8	1599.3
ν(C=C)	1628.3	1626.5	1604.6	1613.3	1625.6	1645.4

3.2. ^{1}H NMR calculation

Nowadays, NMR is one of the most widely applied spectroscopic technique thanks to its high sensitivity and fair results that it provides. Since recently, theoretical prediction of NMR spectral with respect to DFT tends to supplant experimental work. Therefore, ^{1}H NMR of the four complexes was calculated both in gas and condensed phases at B3LYP/LANL2DZ level. The condensed phases were both methanol and chloroform solutions seeing that experimentally $RuCl_2(Azpy)_2$ and $RuCl_2(Nazpy)_2$ are soluble therein. Therefore, these calculations were performed with IPCM method. In addition, combination of LANL2DZ ECP basis set with 6-31g(d) was also tested in gas phase.

3.2.1 $RuCl_2(Azpy)_2$

This complex was in practice characterized according to many references [8, 14].However, regarding the presence of ruthenium atom, pseudo-potential is for the first time experimented to minimize the relativist effect due to core electrons. Therefore, Table 3 collects the H NMR data of ligand Azpy, γ-Cl and δ-Cl isomers both in gas and in condensed phases. And Figure 4 shows up Azpy ligand involved in complex formation for NMR calculations.

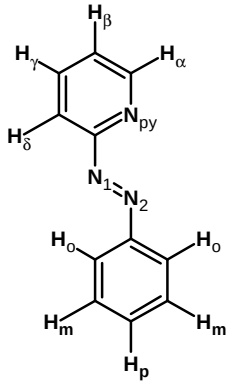

Figure 4: 2-phenylazopyridine(Azpy) for 1H NMR prediction

Table 3: 1H NMR of $RuCl_2(Azpy)_2$ calculated at B3LYP/LANL2DZ level

				LANL2DZ[2]			LANL2DZ[3]			Ru(LANL2DZ)[1]					
^{1}H	LANL2DZ[1]			Methanol			Chloroform			H, C, N, Cl (6-31g(d))			Experimentation[a]		
	Ligand	γ-Cl	δ-Cl	Ligand	γ-Cl	δ-Cl	Ligand	γ-Cl	δ-Cl	Ligand	γ-Cl	δ-Cl	Ligand	γ-Cl	δ-Cl
α	9.38	9.75	9.24	9.19	9.91	9.21	9.39	9.91	9.21	8.73	5.91	7.03	8.65	8.86	7.66
β	7.79	7.96	7.57	8.07	8.49	8.02	8.08	8.49	7.87	7.02	6.30	6.16	7.33	7.76	7.10
γ	8.46	8.56	8.31	8.72	9.04	8.79	8.74	9.04	8.66	7.74	6.95	6.82	7.84	8.11	7.87
δ	8.59	8.75	8.78	8.69	9.03	9.08	8.72	9.03	9.00	7.84	6.49	6.41	7.80	8.53	8.48
Ortho	8.79	8.53	9.25	8.68	8.45	9.13	8.80	8.45	9.17	8.02	7.51	9.01	8.00	7.47	8.00
Meta	8.09	7.50	8.17	8.21	7.72	8.42	8.26	7.72	8.85	7.40	7.05	7.71	7.45	6.90	7.58
Para	8.05	7.68	8.24	8.20	7.92	8.57	8.25	7.98	8.47	7.36	6.83	7.55	7.45	7.11	7.46

Complexes and ligand were performed in [1]gas phase, [2]methanol phase or in [3]chloroform phase.[a]Experimentation was undertaken in $CDCl_3$.

As described in the former article[8] and confirmed in Table 3, B3LYP/6-31g(d) level provides with results of ligand Azpy which chemical shifts are consistent with experimental data. Therefore, the most deshielded protons are assumed to be H_α and H_{ortho}. Regarding the isomers, the discrepancy between bothdeals experimentally with the deshielded protons. While γ-Cl displays H_α and $H_\delta$as the most deshielded protons, δ-Cl shows however H_δ and H_{ortho} with the high chemical shifts. Concerning the theoretical data, both isomers and the lonely ligand present H_α as the

most deshielded proton withB3LYP/LANL2DZ.Moreover, γ-Cl and δ-Cl isomers also show respectively $H_{\delta}$and H_{ortho} as the second most deshielded protons in addition to H_{α}. In Condensed phases, almost the same results are obtained. However, comparatively to gas phase results, they display high chemical shifts. Here, gas phase displays chemical shifts close to the experimental data. Concerning the separated basis set, they alter significantly the chemical shift even if they almost respect the deshielding order in the complexes. Therefore, they are not suitable to characterize the ruthenium complexes since they display inconsistent data with experimental ones as shown in Table 3.

3.2.2. $RuCl_2(Nazpy)_2$

This complex was for the first time synthesized and characterized by Bamba et al [13].Therein, only one complex named α-Cl was obtained and characterized. Figure 5 presents the ligand Nazpy which does not reveal any symmetry regarding protons. Therefore, Table 6 displays chemical shifts predicted at different basis set on ligand Nazpy. So far, NMR calculation was performed either with a pseudo-potential LANL2DZ or on the separate basis set comprising to ECPs basis set. Within Table 4, 6-31g(d) basis set remains one of the suitable functions to provide accurate chemical shift of molecules comprising small atoms. Besides, LANL2DZ pseudo-potential gives for both ligand and complexes consistent data. Moreover, comparatively to experimental data, we can assume that the isomer synthesized in reference 13 corresponds to δ-Cl which results match regardless the phase used. In addition, the results seem to be more accurate in gas phase than in condensed phase. Here, the most deshielded protons are H_{α} and H_6. As summary, we can assume that LANL2DZ pseudo-potential provides with truthful chemical shifts when calculation is performed on molecules comprising Ru atom. It minimizes in fact the relativistic effects created by core electrons of ruthenium atom.

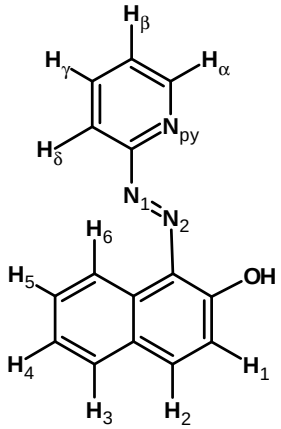

Figure 5: 2-pyridylazonaphtol(Nazpy) for ^{1}H NMR prediction

Tableau 4: 1H NMR of $RuCl_2(Nazpy)_2$ calculated at B3LYP/LANL2DZ level

				LANL2DZ[2]			LANL2DZ[3]			Ru(LANL2DZ)[1]				
^{1}H	LANL2DZ[1]			Methanol			Chloroform			H, C, N, O, Cl (6-31g(d))			Experimentation[a]	
	Ligand	γ-Cl	δ-Cl	Ligand	γ-Cl	δ-Cl	Ligand	γ-Cl	δ-Cl	Ligand	γ-Cl	δ-Cl	Ligand	Complex
α	9.23	8.84	9.82	9.19	10.02	9.67	9.39	9.97	9.69	8.67	5.60	7.95	8.41	8.87
β	7.66	8.67	7.84	8.02	8.62	7.92	8.02	8.47	7.79	6.97	6.44	6.08	7.12	7.72
γ	8.28	8.07	8.49	8.65	9.16	8.9	8.66	9.02	8.76	7.67	6.98	6.79	7.81	8.43
δ	8.41	9.91	8.97	8.57	9.09	8.98	8.60	9.03	8.92	7.69	6.74	6.59	7.88	8.44
1	6.86	6.66	8.08	7.41	6.67	8.35	7.43	6.66	8.33	6.59	5.81	7.48	6.70	7.11
2	7.88	7.78	8.26	8.27	8.07	8.73	8.25	8.02	8.63	7.59	7.27	7.67	7.64	8.32
3	7.73	7.84	7.97	8.04	8.15	8.44	8.03	8.05	8.33	7.42	7.72	7.49	7.92	8.08
4	7.68	7.84	7.79	7.91	8.06	8.16	7.96	7.99	8.08	7.24	7.48	7.30	7.40	8.01
5	8.00	7.90	7.69	8.19	8.03	7.97	8.25	7.98	7.93	7.52	7.63	7.58	7.52	7.90
6	9.63	8.61	8.25	9.58	8.50	9.06	9.92	8.53	9.10	9.42	8.42	9.07	8.41	8.85

Complexes and ligand were performed in [1]gas phase, [2]methanol phase or in [3]chloroform phase .[a]Experimentation was undertaken in $CDCl_3$.

3.3. Free enthalpy calculation

Variation of free enthalpy ΔG was also calculated in gas phase at B3LYP/LANL2DZ for the four complexes at 298.15K. In general,ΔG deals with stability of molecules and spontaneity of reactions. It is determined according to Figure1 as written down in equation (1) below. Besides, calculation is performed by assuming that the reaction theoretically produces only one isomer.

$$\Delta G° = [G°(RuCl_2(Ligand)_2) + G°(3H_2O) + G°(Cl)] - [G°(RuCl_3, 3H_2O) + 2G°(Ligand)].(1)$$

G° was taken from the output data when frequency calculation is performed [20]. Table 5 collects variation of free enthalpy of both azopyridine ruthenium complexes.Table 5 displays at 298.15K that the most stable of those complexes are δ-Cl isomers. Therefore, considering the big shape of ligands that contain at least 23 atoms, we can assume that the best profitable structure of ruthenium azopyridine complexes is δ-Cl isomers. Subsequently, both ligands are placed in trans position so as to minimize their repulsion force. However, literature states that the main product in ruthenium-azopyridine complexes is γ-Cl isomer due certainly to the boiling process at high temperature to synthesize the complex [3, 15, 21-23].Therefore, when focusing on reaction of Figure 2, the dominate isomer is still γ-Cl.

Table 5: Free enthalpy calculation in kcal.mol^{-1} at B3LYP/LANL2DZ level in gas phase at 298°K

Complex	$RuCl_2(Azpy)_2$		$RuCl_2(Nazpy)_2$	
	γ-Cl	δ-Cl	γ-Cl	δ-Cl
ΔG°(kcal.mol^{-1})	-8.64	-9.55	-24.73	-28.87

CONCLUSION

The optimization at B3LYP/LANL2DZ level shows up that the most stable isomer was γ-Cl with the shortest Ru-Ligand lengths in $RuCl_2(Azpy)_2$ and $RuCl_2(Nazpy)_2$.Moreover, that isomer displays a C_2 axis through the bisector of N_{py}-Ru-N_{py} angle that make both azopyridine ligands and both chlorine atoms identical. Whereas δ-Cl, it displays the shortest with an invariable azo length and also a C_2 axis comprising both chlorine and ruthenium atoms. It presents only one plan parallel to the C_2 axis that permits both ligands to be identical. Herein, both chlorine atoms are not equal knowing that the isomer displays two Ru-Cl bondings length. Nevertheless, δ-Cl isomers are admitted to also be a C_2 type.The ^{1}H NMR calculation shows up an obvious discrepancy between γ-$RuCl_2(Azpy)_2$ and δ-$RuCl_2(Azpy)_2$. Withinγ-$RuCl_2(Azpy)_2$, the most deshielded protons are H_α and H_δ. However in δ-$RuCl_2(Azpy)_2$, the deshielded protons are H_α and H_{ortho}. Those results were confirmed regardless the basis set used. Besides, the consistent data with experiment were obtained when calculations were performed with B3LYP/LANL2DZ in gas phase. Moreover, comparatively to experimental data, the chemical shifts displayed with a separate basis set were far from consistency. Regarding $RuCl_2(Nazpy)_2$, ^{1}H NMR prediction shows that the most probable complex is isomer δ-$RuCl_2(Nazpy)_2$since both experimental and theoretical data are consistent. Furthermore, variation of free enthalpy prediction highlights anyway that the most stable isomer is δ-Cl that minimizes repulsion between both hindered ligands at 298.15K. However, the main product yielded by heating in reflux is admitted to beγ-Cl. This means that the stability of the complex depends on temperature.

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